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Courier Press, Leamington Spa, England.

## Description

The present invention relates generally to polyvinyl alcohol compositions useful for making packaging films and the like, and more particularly to polyvinyl alcohol compositions with an additional component therein having improved tensile strength and impact resistance when formed into films.

Polyvinyl alcohol compositions are known and useful for a variety of applications. For example, polyvinyl alcohol films are used in packaging materials, such as granulated laundry detergent and pulverulent pesticides and insecticides. Packages prepared from these films separate the contents from exposure to the immediate surroundings and provide premeasured amounts of the packaged materials.

Polyvinyl alcohol compositions are water soluble, and rapidly dissolved in hot water. Thus, packages with materials designed for being slurried, dispensed or dissolved in water may be conveniently added to hot water, such as to the wash water of a washing machine when the package contains a laundry aid. As the package dissolves, the contents are dispensed.

However, polyvinyl alcohol film are brittle at low temperatures and low relative humidities. They have thus not found wide commercial use as soluble films in packaging consumer products which may be stored under conditions conducive to package breakage prior to use.

U.S. Patent 4,115,292, inventors Richardson et al., issued September 19, 1978, discloses packets of detergent composition in polyvinyl alcohol films which are useful in automatic dishwashers. U.S. Patent No. 3,892,905, inventor Albert, issued July 1, 1975 and U.S. Patent No. 4,155,971, inventor Wysong, issued May 22, 1979, both disclose polyvinyl alcohol film-forming compositions which dissolve in cold water. The former compositions are made from a polymer mixture of polyvinyl alcohol or polyvinyl pyrrolidone and a water-soluble plasticizer such as glycerol or polyethylene glycol. The latter discloses polyvinyl alcohol compositions including polyethylene glycol plasticizers which are said to impart enhanced resistance to package breakage.

U.K. Patent application 2,090,603A, published July 14, 1982, inventor Sonenstein, discloses water soluble films comprising a uniform or homogeneous blend of water soluble polyvinyl alcohol and polyacrylic acid. The compositions are said to have high rates of solubility in both cold and hot water and to be of reduced sensitivity to humidity.

Nevertheless, the known water-soluble polyvinyl alcohol films useful as packaging or delivery pouches have continued to present problems or brittleness at low temperatures and low relative humidities.

Accordingly, it is an object of the present invention to provide polyvinyl alcohol compositions which may be formed into films having greatly enhanced impact resistance at low temperatures and low relative humidities.

It is another object that the inventive polyvinyl alcohol compositions be suitable for forming water soluble or dispersible films for non-aqueous liquids, such as detergents having substantially no free water, as well as for packaging granulated or pulverulent materials.

The present invention relates to a self-supporting film characterised in that it comprises:

a polymeric matrix, the polymeric matrix including polyvinyl alcohol and having a molecular weight from 10,000 to 100,000; and

a plurality of microdomains dispersed throughout the polymeric matrix and being at least partially incompatible with the polyvinyl alcohol, the microdomains being from 0.5 to 10 microns ( $\times 10^{-6}$ m) in size, the microdomains consisting essentially of a rubbery material having a glass transition temperature of less than 0°C and being at least 3 wt % of the film, the polyvinyl alcohol of the polymeric matrix being in a weight ratio with respect to the plurality of microdomains of between 19:1 to 6:1.

In one aspect of this invention, a sealed envelope comprises:

a self-supporting film, the film formed by a polymeric matrix comprising at least 50 wt % polyvinyl alcohol having a plurality of microdomains dispersed there throughout, the polyvinyl alcohol having a molecular weight of from 10,000 to 100,000, the plurality of microdomains consisting essentially of a rubbery material which is at least partially incompatible with the polyvinyl alcohol and has a glass transition temperature of less than 0°C, the microdomains being at least 3 wt. % of the film and the polyvinyl alcohol of the polymeric matrix being in a weight ratio with respect to the plurality of microdomains of between 19:1 and 6:1. Such an envelope may contain a liquid detergent which has substantially no free water.

In another aspect of the present invention, an aqueous polymer composition castable as a thin, self-supporting film comprises:

a polyvinyl alcohol component and a rubber component, the polyvinyl alcohol component having a molecular weight from 10,000 to 100,000 and being 70% to 100% hydrolyzed, the rubber component having a glass transition temperature of less than 0°C and being at least partially incompatible when cast in film form with the polyvinyl alcohol component; and

an aqueous solution in which the polyvinyl alcohol component and the rubber component are dispersed.

In a further aspect, an article useful for treating fabrics comprises:

a flexible pouch, the pouch being resistant to breakage at low temperature and low relative humidity, the pouch formed by a plastic phase and a rubber phase, the plastic phase including polyvinyl alcohol and being in an amount of from 70 wt % to 97 wt % of the pouch, the rubber phase being at least partially

incompatible with the polyvinyl alcohol and having a glass transition temperature at or below  $-18^{\circ}\text{C}$  and being in an amount of from at least 3 wt % to 30 wt % of the pouch, and the rubber phase being in a weight ratio with respect to the plastic phase of from 19:1 to 6:1; and

a laundering aid disposed within the pouch.

Articles made from compositions in accordance with the present invention are resistant to breakage at low temperature and low relative humidity, and are particularly suitable as packaging or delivery pouches for products such as granulated or non-aqueous, liquid laundry detergents. Articles made from these films are preferably water-soluble, or dispersible, and when containing a laundry aid may be conveniently added to the wash water with the film dissolving and dispensing the article's contents.

Another aspect of the present invention relates to a self-supporting film characterised in that it comprises:

a polymeric matrix, the polymeric matrix including polyvinyl alcohol of a molecular weight from 10,000 to 100,000; and

a plurality of microdomains dispersed throughout the polymeric matrix, the microdomains being from 0.5 to 10 microns ( $\times 10^{-6}\text{m}$ ) in size, the microdomains having a glass transition temperature of less than  $0^{\circ}\text{C}$ , the microdomains being at least 3 wt % of the film, the polyvinyl alcohol of the polymeric matrix being in a weight ratio with respect to the plurality of microdomains of between 19:1 to 6:1.

Also, the present invention provides a method of increasing the tensile strength of polyvinyl alcohol films characterised in that it comprises:

providing a polyvinyl alcohol solution, the polyvinyl alcohol having a molecular weight of from 10,000 to 100,000;

admixing a rubber solution with the polyvinyl alcohol solution, the rubber solution being at least partially incompatible with the polyvinyl alcohol solution; and

casting the admixture such that a self-supporting film forms in which the polyvinyl alcohol has formed a polymeric matrix and the rubber solution has formed a plurality of microdomains throughout the polymeric matrix, the polyvinyl alcohol of the polymeric matrix being in a weight ratio with respect to the plurality of microdomains of between 19:1 to 6:1.

The invention will be further explained with reference to the following detailed description, which includes mention of photomicrographs in which:

FIG 1 illustrates a prior art film at a magnification of 1600 times; and

FIG 2 illustrates a film in accordance with the present invention at a magnification of 1600 times.

Polyvinyl alcohol is an excellent film forming material, and has good strength and pliability under most conditions. Polyvinyl alcohol film formation occurs readily by simply evaporating water from the solution.

Commercially available polyvinyl alcohol compositions for casting as films vary in molecular weight and degree of hydrolysis. For most film applications, molecular weights in the range of 10,000 to 100,000 are used. Hydrolysis is the percent by which acetate groups of the polyvinyl alcohol have been substituted with hydroxyl. For film applications, the range of hydrolysis typically is 70% up to 100%. Thus, the term "polyvinyl alcohol" usually includes polyvinyl acetate compounds.

Like other polymeric materials, polyvinyl alcohol can be characterised by glass transition temperature (T<sub>g</sub>). The glass transition temperature is the temperature at which amorphous domains of a polymer take on characteristic properties of the glassy state — brittleness, stiffness and rigidity. At temperature above T<sub>g</sub>, localised, or segment, movement of the polymer macromolecules occurs and the polymer becomes ductile.

Temperature alone does not determine the point at which polyvinyl alcohol becomes brittle, since polyvinyl alcohol readily absorbs water from the atmosphere. The absorbed water acts as a plasticizer, and assists in preventing brittleness. However, at low temperatures and low relative humidity polyvinyl alcohol becomes brittle and has very little impact resistance. Even at  $20^{\circ}\text{C}$ , polyvinyl alcohol becomes brittle when the relative humidity is less than 15%, and at lower temperatures the situation is exacerbated. FIG 1 illustrates the photomicrograph taken by a scanning electron microscope of a prior art polyvinyl alcohol film. As may be seen by FIG 1, the polyvinyl alcohol film has a homogeneous texture and has fractured along a plurality of curves.

A wide variety of materials are known and used as plasticizers for polyvinyl alcohol. For example, ethylene glycol, polyethylene glycol, glycerin and other ether polyols have been known as useful to impart various properties to the films. But plasticizers have not satisfactorily overcome the brittleness problem at low temperatures and relative humidities. And especially after contact with liquids, plasticizer depletion from a polyvinyl alcohol film has been found to present a serious problem.

Broadly, the present invention provides polyvinyl alcohol films which have been toughened by a plurality of discrete, rubbery microdomains. Films in accordance with the invention are resistant to breakage at low temperature and low relative humidity, and may be formed into shapes such as envelopes or pouches (typically having wall thicknesses of from 0.05 mm to 0.5 mm) and sealed by means such as heat or pressure after moistening.

FIG 2 illustrates a film in accordance with the present invention. As may be seen, there are a plurality of microdomains, or phase separated, heterogeneous areas, dispersed throughout the polyvinyl matrix, by contrast to the homogeneous, or single phase, of the prior polyvinyl alcohol film illustrated by FIG 1. The scale of both FIGS 1 and 2 is whereby about 1.5 centimeters represents 10 microns ( $1 \times 10^{-6}\text{m}$ ).

The microdomains in accordance with compositions of the invention have a glass transition temperature of less than 0°C, and more preferably below -18°C. Thus, even under very cold conditions, the microdomain material is rubbery. The discrete microdomains are generally of a size less than 10 microns ( $1 \times 10^{-5}$ m), more preferably between 0.5 to 2 microns ( $\times 10^{-6}$ m), and most preferably 0.5 to 1 micron ( $\times 10^{-6}$ m).

Suitable rubbery materials for microdomains in accordance with the present invention include polydimethylsiloxane ( $T_g = -123^\circ\text{C}$ ), polyethylene ( $T_g = -115^\circ\text{C}$ ), polyoxymethylene ( $T_g = -85^\circ\text{C}$ ), natural rubber ( $T_g = -73^\circ\text{C}$ ), polyisobutylene ( $T_g = -73^\circ\text{C}$ ), poly(ethylene oxide) ( $T_g = -67^\circ\text{C}$ ), neoprene ( $T_g = -50^\circ\text{C}$ ), styrene-butadiene copolymer ( $T_g = -48^\circ\text{C}$ ), polypropylene ( $T_g = -20^\circ\text{C}$ ), poly(vinyl fluoride) ( $T_g = -20^\circ\text{C}$ ), poly(vinylidene chloride) ( $T_g = -19^\circ\text{C}$ ) and acrylate ( $T_g =$  from  $-18^\circ\text{C}$  to  $-43^\circ\text{C}$ , depending upon percent acid groups). Preferred rubbery materials are acrylate and styrene-butadiene copolymer.

The rubbery material, or rubber component, will be at least 3 wt % of films in accordance with the present invention, more preferably from 5 wt % to 15 wt %, and most preferably 5 wt % to 10 wt %.

The microdomains are dispersed in a polymeric matrix comprising at least 50 wt % polyvinyl alcohol, more preferably polyvinyl alcohol in an amount of from 70 wt % to 97 wt %. The polyvinyl alcohol component of the polymeric matrix is preferably in a weight ratio with respect to the plurality of microdomains, or rubber component, of between 32:1 to 2.3:1, more preferably between 19:1 to 6:1.

Films in accordance with the present invention may be prepared from aqueous polymer compositions comprising a polyvinyl alcohol component and a rubber component. The polyvinyl alcohol component preferably has a molecular weight from 10,000 to 50,000, and is 70% to 100% hydrolyzed. Where the films are desirably water soluble, or dispersible, then hydrolysis is preferably 80% to 90%. The rubber component (which forms the discrete microdomains in the film when cast) is at least partially incompatible with the polyvinyl alcohol component.

It is believed that microdomains of the inventive films improve tensile strength and impact resistance, particularly at low temperatures and relative humidities, by permitting microscopic "crazing" of the polymer matrix adjacent the microdomains when the films are subject to deformation.

Aqueous polymer compositions in accordance with the invention may include dispersing agents, such as sorbitol, mannitol, dextran, glycerin, and one or more wetting agents, such as non-ionic surfactants or the like.

Example I, below, illustrates an aqueous polymer composition embodiment of the invention and the formation of a thin, self-supporting film cast therefrom.

#### Example I

The rubber component was provided by CarboSet 515 (acrylate polymer having about 8% acid groups before neutralization and a  $T_g$  of  $-18^\circ\text{C}$ , available from B.F. Goodrich). 40 parts of the CarboSet 515 were added with vigorous agitation to a solution containing 2.0 parts of concentrated ammonia (for neutralization of acid groups), 0.5 parts of non-ionic surfactant (Triton X-114 available from Rohm and Haas Co.) and 57.5 parts of demineralized water. The CarboSet 515 dissolved in about one hour with pH at 7.7. The resultant rubber component solution was a clear, viscous syrup ( $\eta = 600$  cps/mPa.s at 20 rpm, No. 3 spindle of a Brookfield viscometer).

The polyvinyl alcohol component was provided by an 88% hydrolyzed, 10,000 molecular weight polymer from Aldrich Chemical Co. One part of non-ionic surfactant (Triton X-114) was dissolved in 79 parts of demineralized water and the solution heated to  $80^\circ\text{C}$  with agitation. Twenty parts of the polyvinyl alcohol were then added slowly in several portions to avoid particle agglomeration. The resultant polyvinyl alcohol solution was a clear, viscous syrup ( $\eta = 600$  cps/mPa.s at 20 rpm, No. 3 spindle of a Brookfield viscometer).

A dispersing solution was prepared by dissolving 50 parts of sorbitol in 50 parts of demineralized water.

Two parts of the dispersing solution, 2.5 parts of the rubber component solution and 40 parts of the polyvinyl alcohol component solution were admixed with gentle stirring to avoid generating bubbles. The admixture (a cloudy emulsion) was then cast as a 2.4 mil ( $\sim 0.0061$  cm) thick film on a glass plate and the film dried at about  $50^\circ\text{C}$  or above.

The photomicrograph of FIG 2 was taken of a film prepared as just-described in Example I. This film embodiment will sometimes hereinafter be referred to as the "Example I embodiment", and is a preferred embodiment.

Films of the invention are typically hazy (due to the phase separation between microdomains and polymeric matrix) and show two sets of glass transition temperatures. One glass transition is attributable to the rubber component, or rubbery phase, and the other to the polyvinyl alcohol component, or polymer phase. The latter typically varies depending upon relative humidity, but is at a significantly higher temperature than the former. For example, differential scanning calorimetry of the Example I embodiment at a heating rate of  $5^\circ\text{C}$  per minute (conducted over a temperature range between  $-40^\circ\text{C}$  to  $60^\circ\text{C}$ ) and at 40% relative humidity, showed a  $T_g$  of between  $-31^\circ\text{C}$  to  $-21^\circ\text{C}$  (attributable to the rubber component, or microdomains), and then another  $T_g$  of about  $28^\circ\text{C}$  attributable to the polyvinyl alcohol matrix.

In an analogous manner, other inventive film embodiments were prepared utilizing various rubber components to form the dispersed microdomains. For example, inventive, toughened polyvinyl alcohol

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films were prepared with another acrylate polymer (Hycar 2600 X 171, having about 4.5% acid groups before neutralization, Tg of  $-43^{\circ}\text{C}$ , available from B.F. Goodrich), with a styrene-butadiene copolymer (Goodright 2505, Tg of  $-48^{\circ}\text{C}$ , available from B.F. Goodrich), with isoprene polymer (Hartex 102, Tg of  $-70^{\circ}\text{C}$ , available from Firestone Rubber Co.) and with a chloroprene polymer (i.e. neoprene, Tg of  $-50^{\circ}\text{C}$ , available from Firestone Rubber Co.).

Resistance to breakage at different temperatures and relative humidities for films in accordance with the present invention are illustrated by Tables I and II, below. The data of both Tables was gathered by testing at least ten samples of the Example I embodiment by dropping a metal dart of a fixed weight from increasing heights until the film being tested ruptured. Films were conditioned at specified R.H. and temperature before being tested, and the impact tests were performed in a constant temperature room. The tested films had a film thickness of 2.1 mil ( $\sim 0.0053$  cm).

TABLE I

	Temp. ( $^{\circ}\text{C}$ )	R.H.	dart wt. (g)	height (cm) for rupture
	-17.8	<20%	55	15.24
	4.4	20%	55	15.24
	4.4	35%	120	17.78
	23.9	50%	>315	38.10
	32.2	85%	>400	38.10
	37.8	70%	>315	38.10

For comparison, polyvinyl alcohol films with plasticizer (6 wt.% trimethylpropane) but without the rubber component (that is, without microdomains) were also tested under the same sets of temperature and relative humidity conditions as in Table I. At  $-17.8^{\circ}\text{C}$  (R.H. of less than 20%) the comparison films were too brittle to test and at  $4.4^{\circ}\text{C}$  (R.H. of 20%) the comparison films ruptured when a 55 gram dart impacted the films after falling from a height of about 10 centimeters. That is, the inventive films demonstrated significantly improved impact resistance at low temperatures and low relative humidities with respect to the comparison, polyvinyl alcohol films. The impact resistances of both the inventive films and the comparison films were similar at temperatures at and above about  $23.9^{\circ}\text{C}$  ( $75^{\circ}\text{F}$ ) and R.H. of 50% or higher. Table II, below, illustrates data from tests similar to those illustrated by Table I, but with the difference that the inventive films were exposed for 12 days to a liquid laundry detergent before the impact testing.

TABLE II

	Temp. ( $^{\circ}\text{C}$ )	R.H.	dart wt. (g)	height (cm) for rupture
	4.4	20%	55	20.32
	4.4	35%	55	20.32
	23.9	50%	> 315	38.10
	32.2	85%	> 454	38.10
	37.8	70%	> 245	38.10

As illustrated by the data of Table II, above, the inventive films were more resistant to impact after having been exposed to detergent than without such exposure at low temperatures and R.H. and generally retain impact resistance after detergent exposure over a very wide range of temperature and relative humidity conditions. By contrast, comparison polyvinyl alcohol films exposed to detergent for 12 days were ruptured at  $4.4^{\circ}\text{C}$  (and R.H. of 20%) by the 55 gram dart's falling from a height of only about 2.54 cm. It is believed that this may be due to plasticizer migration from the comparison films into the detergent.

The tensile strength and percent elongation of the Example I embodiment were also determined based on American Standards Testing Materials method at a two inch (5.08 cm) per minute cross head speed, with 35% R.H. and  $21.1^{\circ}\text{C}$ , and were found to have substantially improved tensile strength and elongation properties with respect to comparison polyvinyl alcohol films. Table III, below, illustrates the data of two

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different embodiments of the invention and of a comparison film (including plasticizer but no rubber component), all of which were tested for tensile strength and elongation.

TABLE III

	Tensile at Failure	
	(p.s.i./kg.sq.cm <sup>-1</sup> )	Elongation(%)
inventive film (a)*	4500/316.4	640
inventive film (b)**	4300/302.3	700
comparison film ***	2300/161.7	650

- \* 85 wt.% polyvinyl alcohol component, 10 wt.% rubber component, 5 wt.% sorbitol, 3.2 mil (~0.0081 cm) thickness  
 \*\* 76 wt.% polyvinyl alcohol component, 10 wt.% rubber component, 10 wt.% sorbitol, 4 wt.% wetting agent (Triton X 114), 2.4 mil (~0.0061 cm) thickness  
 \*\*\* 78 wt.% polyvinyl alcohol, 8.8 wt.% sorbitol, 6 wt.% trimethylpropane, 6 wt.% glycerin, 1 wt.% wetting agent (Triton X 114), 2.5 mil (~0.0064 cm) thickness

As can be seen from the Table III data, above, a comparison polyvinyl alcohol film tested at the same temperature and relative humidity conditions had significantly less tensile strength and about the same percent elongation properties as the inventive film embodiments.

Samples of the Example I embodiment were also studied for time to disperse and to dissolve by testing in a standard laundry solution (including Borate) at 21.1°C. The films broke up and completely dissolved in less than 30 seconds.

## Claims

1. A self-supporting film characterised in that it comprises:  
 a polymeric matrix, the polymeric matrix including polyvinyl alcohol and having a molecular weight from 10,000 to 100,000; and  
 a plurality of microdomains dispersed throughout the polymeric matrix and being at least partially incompatible with the polyvinyl alcohol, the microdomains being from 0.5 to 10 microns ( $\times 10^{-6}$ m) in size, the microdomains consisting essentially of a rubbery material having a glass transition temperature of less than 0°C and being at least 3 wt % of the film, the polyvinyl alcohol of the polymeric matrix being in a weight ratio with respect to the plurality of microdomains of between 19:1 to 6:1.
2. A film as claimed in claim 1 wherein a thickness thereof is from 0.05 to 0.5 mm.
3. A sealed envelope characterised in that it comprises:  
 a self-supporting film, the film formed by a polymeric matrix comprising at least 50 wt % polyvinyl alcohol and having a plurality of microdomains dispersed there throughout, the polyvinyl alcohol having a molecular weight of from 10,000 to 100,000, the plurality of microdomains consisting essentially of a rubbery material which is at least partially incompatible with the polyvinyl alcohol and has a glass transition temperature of less than 0°C, the microdomains being at least 3 wt % of the film and the polyvinyl alcohol of the polymeric matrix being in a weight ratio with respect to the plurality of microdomains of between 19:1 to 6:1.
4. A film or envelope as claimed in any of claims 1 to 3 wherein the microdomains are from 5 wt % to 15 wt % of the film.
5. A film or envelope as claimed in any of claims 1 to 4 wherein substantially all of the microdomains are less than 10 microns ( $1 \times 10^{-5}$ m) in size.
6. A film or envelope as claimed in claim 5 wherein at least most of the microdomains are from 0.5 to 2 microns ( $\times 10^{-6}$ m) in size.
7. A film or envelope as claimed in any of claims 1 to 6 wherein the rubbery material of the microdomains has a glass transition temperature of -18°C or less.
8. An envelope as claimed in any of claims 3 to 7 containing a liquid detergent which has substantially no free water.
9. An article useful for treating fabrics characterised in that it comprises:  
 a flexible pouch, the pouch being resistant to breakage at low temperature and low relative humidity, the pouch formed by a plastic phase and a rubber phase, the plastic phase including polyvinyl alcohol and being in an amount of from 70 wt % to 97 wt % of the pouch, the rubber phase being at least partially incompatible with the polyvinyl alcohol and having a glass transition temperature at or below -18°C and being in an amount of from at least 3 wt % to 30 wt % of the pouch, and the rubber phase being in a weight ratio with respect to the plastic phase of from 19:1 to 6:1; and  
 a laundering aid disposed within the pouch.



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10. An envelope or article as claimed in any of claims 3 to 9 wherein:  
the polyvinyl alcohol has a molecular weight of from 10,000 to 100,000 and is 70% to 100% hydrolyzed.
11. An envelope or article as claimed in any of claims 3 to 10 wherein:  
the rubber phase comprises polysiloxane, polyethylene, polyoxymethylene, neoprene, isoprene,  
5 natural rubber, acrylate, styrene-butadiene copolymer, polyisobutylene, polypropylene, polyvinyl fluoride,  
polyvinylidene chloride or mixtures thereof.
12. An envelope or article as claimed in any of claims 3 to 11 wherein a wall of the envelope or pouch  
has a thickness of from 0.05 mm to 0.5 mm.
13. An envelope or article as claimed in any of claims 3 to 12 wherein the envelope or pouch is soluble  
10 or dispersible in water or an aqueous solution.
14. An aqueous polymer composition castable as a thin, self-supporting film characterised in that it  
comprises:  
a polyvinyl alcohol component and a rubber component, the polyvinyl alcohol component having a  
molecular weight from 10,000 to 100,000 and being 70% to 100% hydrolyzed, the rubber component  
15 having a glass transition temperature of less than 0°C and being at least partially incompatible when cast in  
film form with the polyvinyl alcohol component; and  
an aqueous solution in which the polyvinyl alcohol component and the rubber component are  
dispersed.
15. A polymer composition as claimed in claim 14 wherein the aqueous solution includes sorbitol,  
20 mannitol, dextran, glycerin, a wetting agent or mixtures thereof.
16. A self-supporting film characterised in that it comprises:  
a polymeric matrix, the polymeric matrix including polyvinyl alcohol of a molecular weight from 10,000  
to 100,000; and  
a plurality of microdomains dispersed throughout the polymeric matrix, the microdomains being from  
25 0.5 to 10 microns ( $\times 10^{-6}$ m) in size, the microdomains having a glass transition temperature of less than  
0°C, the microdomains being at least 3 wt % of the film, the polyvinyl alcohol of the polymeric matrix being  
in a weight ratio with respect to the plurality of microdomains of between 19:1 to 6:1.
17. A method of increasing the tensile strength of polyvinyl alcohol films characterised in that it  
comprises:  
30 providing a polyvinyl alcohol solution, the polyvinyl alcohol having a molecular weight of from 10,000  
to 100,000;  
admixing a rubber solution with the polyvinyl alcohol solution, the rubber solution being at least  
partially incompatible with the polyvinyl alcohol solution; and  
casting the admixture such that a self-supporting film forms in which the polyvinyl alcohol has formed  
35 a polymeric matrix and the rubber solution has formed a plurality of microdomains throughout the  
polymeric matrix, the polyvinyl alcohol of the polymeric matrix being in a weight ratio with respect to the  
plurality of microdomains of between 19:1 to 6:1.

### Patentansprüche

- 40 1. Selbsttragender Film, dadurch gekennzeichnet, daß er folgendes umfaßt:  
eine polymere Matrix, wobei die polymere Matrix Polyvinylalkohol einschließt und ein Mole-  
kulargewicht von 10.000 bis 100.000 hat; und  
eine Vielzahl von Mikrobereichen, die durch die polymere Matrix hindurch dispergiert sind und  
45 mindestens teilweise mit dem Polyvinylalkohol unverträglich sind, wobei die Größe der Mikrobereiche 0,5  
bis 10 Mikron ( $\times 10^{-6}$ m) beträgt, wobei die Mikrobereiche im wesentlichen aus einem kautschukartigen  
Material mit einer Glasübergangstemperatur von weniger als 0°C bestehen und mindestens 3 Gew.-% des  
Films ausmachen und wobei der Polyvinylalkohol der polymeren Matrix in einem Gewichtsverhältnis  
bezogen auf die Vielzahl der Mikrobereiche von zwischen 19:1 bis 6:1 vorliegt.
- 50 2. Film nach Anspruch 1, dadurch gekennzeichnet, daß seine Dicke 0,05 bis 0,5 mm beträgt.
3. Verschlüssener Umschlag, dadurch gekennzeichnet, daß er folgendes umfaßt:  
einen selbsttragenden Film, wobei der Film aus einer polymeren Matrix gebildet ist, die mindestens 50  
Gew.-% Polyvinylalkohol enthält und eine Vielzahl von durch sie hindurch dispergierten Mikrobereichen  
aufweist, wobei der Polyvinylalkohol ein Molekulargewicht von 10.000 bis 100.000 hat, die Vielzahl von  
55 Mikrobereichen im wesentlichen aus einem kautschukartigen Material besteht, das mindestens teilweise  
mit dem Polyvinylalkohol unverträglich ist und eine Glasübergangstemperatur von weniger als 0°C hat, die  
Mikrobereiche wenigstens 3 Gew.-% des Films ausmachen und der Polyvinylalkohol der polymeren Matrix  
in einem Gewichtsverhältnis bezogen auf die Vielzahl der Mikrobereiche von zwischen 19:1 bis 6:1 vorliegt.
4. Film oder Umschlag nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die  
60 Mikrobereiche 5 Gew.-% bis 15 Gew.-% des Films ausmachen.
5. Film oder Umschlag nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß im  
wesentlichen alle Mikrobereiche eine Größe von weniger als 10 Mikron ( $1 \times 10^{-6}$ m) haben.
6. Film oder Umschlag nach Anspruch 5, dadurch gekennzeichnet, daß mindestens die meisten der  
Mikrobereiche eine Größe von 0,5 bis 2 Mikron ( $\times 10^{-6}$ m) haben.
- 65 7. Film oder Umschlag nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das

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kautschukartige Material der Mikrobereiche eine Glasübergangstemperatur von  $-18^{\circ}\text{C}$  oder weniger hat.

8. Umschlag nach einem der Ansprüche 3 bis 7, dadurch gekennzeichnet, daß er ein flüssiges Detergens, das im wesentlichen kein freies Wasser hat, enthält.

9. Zur Behandlung von Stoffen verwendbarer Gegenstand, dadurch gekennzeichnet, daß er folgendes  
5 umfaßt:

einen flexiblen Beutel, wobei der Beutel gegenüber einem Bruch bei niedriger Temperatur und niedriger relativer Feuchtigkeit beständig ist, wobei der Beutel aus einer Kunststoffphase und einer Kautschukphase gebildet ist, wobei die Kunststoffphase Polyvinylalkohol einschließt und in einer Menge von 70 Gew.-% bis 97 Gew.-% des Beutels vorliegt, wobei die Kautschukphase mindestens teilweise mit dem

10 Polyvinylalkohol unverträglich ist und eine Glasübergangstemperatur von  $-18^{\circ}\text{C}$  oder darunter hat und in einer Menge von mindestens 3 Gew.-% bis 30 Gew.-% des Beutels vorliegt und wobei die Kautschukphase im Gewichtsverhältnis bezogen auf die Kunststoffphase von 19:1 bis 6:1 vorliegt; und

ein innerhalb des Beutels angeordnetes Waschlösungsmittel.

10. Umschlag oder Gegenstand nach einem der Ansprüche 3 bis 9, dadurch gekennzeichnet, daß der  
15 Polyvinylalkohol ein Molekulargewicht von 10.000 bis 100.000 hat und zu 70 bis 100% hydrolysiert ist.

11. Umschlag oder Gegenstand nach einem der Ansprüche 3 bis 10, dadurch gekennzeichnet, daß die Kautschukphase Polysiloxan, Polyethylen, Polyoxymethylen, Neopren, Isopren, Naturkautschuk, Acrylat, Styrol-Butadiencopolymeres, Polyisobutylen, Polypropylen, Polyvinylfluorid, Polyvinylidenchlorid oder Gemische davon umfaßt.

20 12. Umschlag oder Gegenstand nach einem der Ansprüche 3 bis 11, dadurch gekennzeichnet, daß eine Wand des Umschlags oder des Beutels eine Dicke von 0,05 mm bis 0,5 mm hat.

13. Umschlag oder Gegenstand nach einem der Ansprüche 3 bis 12, dadurch gekennzeichnet, daß der Umschlag oder der Beutel in Wasser oder einer wäßrigen Lösung löslich oder dispergierbar ist.

25 14. Wäßrige Polymermasse, die als dünner, selbsttragender Film gießbar ist, dadurch gekennzeichnet, daß sie folgendes umfaßt:

eine Polyvinylalkoholkomponente und eine Kautschukkomponente, wobei die Polyvinylalkoholkomponente ein Molekulargewicht von 10.000 bis 100.000 hat und zu 70 bis 100% hydrolysiert ist, wobei die Kautschukkomponente eine Glasübergangstemperatur von weniger als  $0^{\circ}\text{C}$  hat und, wenn sie in Filmform gegossen wird, mindestens teilweise mit der Polyvinylalkoholkomponente

30 unverträglich ist; und eine wäßrige Lösung, in der die Polyvinylalkoholkomponente und die Kautschukkomponente dispergiert sind.

15. Polymermasse nach Anspruch 14, dadurch gekennzeichnet, daß die wäßrige Lösung Sorbit, Mannit, Dextran, Glycerin, ein Befeuchtungsmittel oder Gemische davon enthält.

35 16. Selbsttragender Film, dadurch gekennzeichnet, daß er folgendes umfaßt:

eine polymere Matrix, wobei die polymere Matrix Polyvinylalkohol mit einem Molekulargewicht von 10.000 bis 100.000 einschließt; und

40 eine Vielzahl von Mikrobereichen, die durch die polymere Matrix hindurch dispergiert sind, wobei die Mikrobereiche einer Größe von 0,5 bis 10 Mikron ( $\times 10^{-6}\text{m}$ ) haben, wobei die Mikrobereiche eine Glasübergangstemperatur von weniger als  $0^{\circ}\text{C}$  haben, wobei die Mikrobereiche mindestens 3 Gew.-% des Films ausmachen und wobei der Polyvinylalkohol der polymeren Matrix in einem Gewichtsverhältnis bezogen auf die Vielzahl der Mikrobereiche von zwischen 19:1 bis 6:1 vorliegt.

17. Verfahren zur Erhöhung der Zugfestigkeit von Polyvinylalkoholfilmen, dadurch gekennzeichnet, daß man

45 eine Polyvinylalkohollösung vorsieht, wobei der Polyvinylalkohol ein Molekulargewicht von 10.000 bis 100.000 hat;

mit der Polyvinylalkohollösung eine Kautschuklösung vermischt, wobei die Kautschuklösung mit der Polyvinylalkohollösung mindestens teilweise unverträglich ist; und

50 das Gemisch in der Weise gießt, daß sich ein selbsttragender Film bildet, bei dem der Polyvinylalkohol eine polymere Matrix gebildet hat und die Kautschuklösung eine Vielzahl von Mikrobereichen durch die polymere Matrix hindurch gebildet hat, wobei der Polyvinylalkohol der polymeren Matrix in einem Gewichtsverhältnis bezogen auf die Vielzahl der Mikrobereiche von zwischen 19:1 bis 6:1 vorliegt.

### 55 Revendications

1. Une pellicule autoportante, caractérisée en ce qu'elle comprend:

une matrice polymère, la matrice polymère comprenant de l'alcool polyvinylique et ayant un poids moléculaire de 10 000 à 100 000; et

60 de nombreux microdomaines dispersés dans la matrice polymère et étant au moins partiellement incompatibles avec l'alcool polyvinylique, les microdomaines ayant une taille de 0,5 à 10 micromètres ( $\times 10^{-6}\text{m}$ ), les microdomaines consistant essentiellement en une matière caoutchouteuse ayant une température de transition vitreuse inférieure à  $0^{\circ}\text{C}$  et constituant au moins 3% du poids de la pellicule, l'alcool polyvinylique de la matrice polymère étant dans un rapport pondéral relativement aux nombreux  
65 microdomaines entre 19/1 et 6/1.

2. Une pellicule selon la revendication 1 dont l'épaisseur est de 0,05 à 0,5 mm.
3. Une enveloppe scellée, caractérisée en ce qu'elle comprend:  
une pellicule autoportante, la pellicule étant formée d'une matrice polymère comprenant au moins 50% en poids d'alcool polyvinylique et ayant de nombreux microdomaines qui y sont dispersés, l'alcool polyvinylique ayant un poids moléculaire de 10 000 à 100 000, les nombreux microdomaines consistant essentiellement en une matière caoutchouteuse qui est au moins partiellement incompatible avec l'alcool polyvinylique et a une température de transition vitreuse inférieure à 0°C, les microdomaines constituant au moins 3% du poids de la pellicule et l'alcool polyvinylique de la matrice polymère étant dans un rapport pondérale relativement aux nombreux microdomaines entre 19/1 et 6/1.
4. Une pellicule ou enveloppe selon l'une quelconque des revendications 1 à 3, dans laquelle les microdomaines constituent de 5% à 15% du poids de la pellicule.
5. Une pellicule ou enveloppe selon l'une quelconque des revendications 1 à 4, dans laquelle essentiellement la totalité des microdomaines a une taille inférieure à 10 micromètres ( $1 \times 10^{-6}$ m).
6. Une pellicule ou enveloppe selon la revendication 5, dans laquelle au moins la plupart des microdomaines ont une taille de 0,5 à 2 micromètres ( $\times 10^{-6}$ m).
7. Une pellicule ou enveloppe selon l'une quelconque des revendications 1 à 6, dans laquelle la matière caoutchouteuse des microdomaines a une température de transition vitreuse de -18°C ou moins.
8. Une enveloppe selon l'une quelconque des revendications 3 à 7 contenant un détergent liquide qui n'a essentiellement pas d'eau libre.
9. Un article utile pour le traitement des tissus, caractérisé en ce qu'il comprend:  
un sachet souple, le sachet résistant à la rupture à basse température et en humidité relativement faible, le sachet étant formé d'une phase plastique et d'une phase de caoutchouc, la phase plastique comprenant de l'alcool polyvinylique et étant en une quantité de 70% à 97% du poids du sachet, la phase de caoutchouc étant au moins partiellement incompatible avec l'alcool polyvinylique et ayant une température de transition vitreuse égale ou inférieure à -18°C et étant en une quantité d'au moins 3% à 30% du poids du sachet et la phase de caoutchouc étant dans un rapport pondérale relativement à la phase plastique de 19/1 à 6/1; et  
un aide de lavage disposé dans le sachet.
10. Une pellicule ou enveloppe selon l'une quelconque des revendications 3 à 9 où:  
l'alcool polyvinylique a un poids moléculaire de 10 000 à 100 000 et est hydrolysé de 70% à 100%.
11. Une enveloppe ou un article selon l'une quelconque des revendications 3 à 10 où:  
la phase de caoutchouc comprend un polysiloxane, un polyéthylène, un polyoxyméthylène, du néoprène, de l'isoprène, un caoutchouc naturel, un acrylate, un copolymère de styrène-butadiène, un polyisobutylène, un polypropylène, un fluorure de polyvinyle, un chlorure de polyvinylidène ou leurs mélanges.
12. Une enveloppe ou un article selon l'une quelconque des revendications 3 à 11, où la paroi de l'enveloppe ou du sachet a une épaisseur de 0,05 mm à 0,5 mm.
13. Une enveloppe ou un article selon l'une quelconque des revendications 3 à 12, où l'enveloppe ou sachet est soluble dans l'eau ou une solution aqueuse.
14. Une composition aqueuse de polymère pouvant être coulée sous forme d'une pellicule mince autoportante, caractérisée en ce qu'elle comprend:  
un composant alcool polyvinylique et un composant caoutchouc, le composant alcool polyvinylique ayant un poids moléculaire de 10 000 à 100 000 et étant hydrolysé de 70% à 100%, le composant caoutchouc ayant une température de transition vitreuse inférieure à 0°C et étant au moins partiellement incompatible lorsqu'il est coulé sous forme d'une pellicule avec le composant alcool polyvinylique; et  
une solution aqueuse dans laquelle le composant alcool polyvinylique et le composant caoutchouc sont dispersés.
15. Une composition de polymère selon la revendication 14, dans laquelle la solution aqueuse comprend du sorbitol, du mannitol, du dextran, de la glycérine, un agent mouillant ou leurs mélanges.
16. Une pellicule autoportante, caractérisée en ce qu'elle comprend:  
une matrice polymère, la matrice polymère comprenant de l'alcool polyvinylique ayant un poids moléculaire de 10 000 à 100 000; et  
de nombreux microdomaines dispersés dans la matrice polymère, les microdomaines ayant une taille de 0,5 à 10 micromètres ( $\times 10^{-6}$ m), les microdomaines ayant une température de transition vitreuse inférieure à 0°C, les microdomaines constituant au moins 3% du poids de la pellicule, l'alcool polyvinylique de la matrice polymère étant dans un rapport pondérale relativement aux nombreux microdomaines entre 19/1 et 6/1.
17. Un procédé pour accroître la résistance à la traction de pellicules d'alcool polyvinylique, caractérisé en ce qu'il consiste à:  
se pourvoir d'une solution d'alcool polyvinylique, l'alcool polyvinylique ayant un poids moléculaire de 10 000 à 100 000;  
mélanger une solution de caoutchouc avec la solution d'alcool polyvinylique, la solution de caoutchouc

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étant au moins partiellement incompatible avec la solution d'alcool polyvinylique; et  
couler le mélange pour former une pellicule autoportante dans laquelle l'alcool polyvinylique a formé  
une matrice polymère et la solution de caoutchouc a formé de nombreux microdomaines dans la matrice  
polymère, l'alcool polyvinylique de la matrice polymère étant dans un rapport pondérale relatif aux  
5 nombreux microdomaines entre 19/1 et 6/1.

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FIG. 1.  
(PRIOR ART)



FIG. 2.



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